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Hydrogen production from the steam reforming of liquid hydrocarbons in membrane reactor

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Abstract

Hydrogen production from the steam reforming of liquid hydrocarbons over a self-made nickel catalyst was investigated in a fixed bed palladium membrane reactor (PMR). The reactions were carried out at 723–823 K and 200–900 kPa. The applied Pd membrane was developed by a novel electroless plating method. The influences of working conditions on the performance of the PMR were also studied. The results indicate that the membrane has a H_2 permeance of 50.0 $m^3\ m^{-2}\ h^{-1}\ bar^{-1}$ and a H_2/N_2 separation coefficient of 1200, determined at 773 K and transmembrane pressure of 100 kPa using a single gas method. Owing to the selective removal of H_2 by the membrane, the yield of H_2 greatly increased; meanwhile the yield of CH_4 efficiently decreased. The purity of H_2 in the permeate side of membrane could be maintained over 99.5%. H_2 production capacity of the PMR could be as high as 23.1 $m^3\ m^{-2}\ h^{-1}$ (m^3 H_2 per m^2 membrane area per hour) under optimized working conditions. The reactions in the steam reforming of liquid hydrocarbons and H_2 separation are highly integrated in the PMR, which suggests that the steam reforming of liquid hydrocarbons in PMR could be an attractive process for H_2 production under mild reaction conditions.

Keywords: Hydrogen production; Liquid hydrocarbons; Steam reforming; Palladium membrane reactor; Nickel catalyst

1. Introduction

Hydrogen production is a matter of great importance, both in refinery and clean fuel production recently. However, a renewed interest in its production processes has emerged, driven by the spectacular fuel cell technologies. H_2 is the ideal fuel for polymer electrolyte fuel cells (PEMFC), nowadays being efficiently produced from methane, naphtha, gasoline, diesel and the like [1–3]. Large-scale H_2 production by the steam reforming of methane or naphtha is well established in the chemical industry [2]. An industrial steam reformer typically consists of a fixed bed reactor made up of a large number of catalyst tubes, surrounded by a huge top-/side-fired furnace. Usually, steam reforming of higher hydrocarbons can be represented by the following reactions [4,5]:

$$C_nH_m + nH_2O = nCO + (n + m/2)H_2 \quad \text{(for isooctane}, n = 8, \Delta H^\circ_{298} = 1273\,\text{kJ/mol)} \tag{1}$$

$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \quad (\Delta H^\circ_{298} = -206\,\text{kJ/mol}) \tag{2}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (\Delta H^\circ_{298} = -41.1\,\text{kJ/mol}) \tag{3}$$

Higher hydrocarbons are irreversibly converted into CO and H_2, followed by the fast methanation and water–gas shift reaction (WGS). In a conventional fixed bed reactor (CFBR), although higher hydrocarbons could be completely converted using suitable catalysts at 723–823 K, the yield of CH_4 is controlled by the thermodynamic equilibrium and usually high. Thus, in the traditional naphtha steam reforming process, to achieve an acceptable yield of H_2, it is necessary to carry out the reactions at temperatures up to 1123 K. In addition, the downstream processing of CO by WGS and H_2 purification are also necessary [6]. Thus, the whole process is complicated, and uneconomical for small-scale H_2 production. Therefore, small

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scale H_2 production process requires further investigation to meet the requirements of purity, economy, and versatility for its use in fuel processor systems coupled to fuel cells [7]. The utilization of membrane reactors (MR) is one of the most interesting options to consider, given its advantages related to heat and energy management, and the integration of two different processes (reaction and separation) in a single unit. In the case of steam reforming of higher hydrocarbons, provided that higher hydrocarbons are fully converted and thermodynamic equilibrium established, the use of a hydrogen-permselective membrane could break the thermodynamic equilibrium of methanation (Eq. (2)) and WGS (Eq. (3)) reactions. In this way, H_2 production could be enhanced, while methane formation suppressed. So, it is feasible to avoid the high temperature reactions and the complex downstream processing in the traditional naphtha steam reforming process by using MR.

Pd membranes, whose operation is based on a H_2 solution–diffusion mechanism on a permselective film, could efficiently separate H_2 from the reaction zone. Thus, intensive investigation on their application to reactions such as dehydrogenation, steam reforming and dry reforming has been performed [8–10]. For instance, investigation on methane steam reforming using PMR [8,11–13] suggested that methane conversions much higher than thermodynamically controlled ones could be obtained. However, the steam reforming of liquid hydrocarbons in PMR was seldom experimentally investigated. Recently, Chen et al. [14–17] simulated *n*-heptane steam reforming in a circulating fluidized bed membrane reformer (CFBMR). It was predicted that H_2 could be efficiently produced from the steam reforming of *n*-heptane at 723–823 K. Compared with those obtained in CFBR, the yield of H_2 could be increased by about 300% in the CFBMR.

Owing to the wide availability of fixed bed reactors and their convenience, cheapness and simplicity, H_2 production from the steam reforming of liquid hydrocarbons in a fixed bed PMR was experimentally investigated in this work. It was found that the reactions in the steam reforming of liquid hydrocarbons and H_2 separation could be efficiently integrated in the PMR. Pure H_2 production from the steam reforming of liquid hydrocarbons could be realized at temperatures lower than 823 K using only one fixed bed PMR and one catalyst. Influences of working conditions such as temperature, pressure, steam-to-carbon feed ratios (S/C ratios), gas hourly space velocity (GHSV) and sweep gas flux on the performance of the PMR were also investigated.

2. Experimental

2.1. Pd membrane

The Pd membrane was supported on a porous α-alumina tube by a novel electroless plating method developed in our lab [18]. The support has an o.d. = 10.0 mm, an i.d. = 6.2 mm and a nominal pore size of 500 nm. One end of the membrane is closed. The total length of the tube, the length of the porous part and the effective separation area are 300 mm, 50 mm and 15.7 cm^2, respectively.

2.2. Catalyst

The applied catalyst was prepared by a coprecipitation method. The procedure was described in a previous report [19]. The catalyst was composed of 50.0 wt.% NiO, 10.0 wt.% La_2O_3 and balance alumina, determined by X-ray fluorescence using Magix-601 (Philips). The catalyst was found to show good catalytic performance in the gasoline surrogate steam reforming at about 773 K in a CFBR [19].

2.3. Reaction and instruments

Fig. 1 shows the schematic diagram of the reaction and analysis system. The membrane tube was located at the center of a stainless steel (SS) tube (i.d. = 20 mm), making an annulus reaction chamber (reaction side or retentate side). Graphite O-rings and modified compression fittings afforded leak-free seal at pressures up to 1500 kPa. The volume inside the membrane tube was the permeate side. In the permeate side, a dense SS tube (o.d. = 3 mm) was located near the closed end of the membrane tube for the introduction of a sweep gas flux. The countercurrent operation mode, owing to its superiority over the cocurrent one [17], was applied. A movable thermocouple (o.d. = 1 mm) detected the temperature of the catalyst bed. The pressures in the reaction side were controlled by a backpressure regulator. A precise pressure gauge read the pressures. The permeate side was maintained at atmospheric pressure. In the reaction chamber, 5.5 g catalyst in the grain size range of 420–630 μm, diluted by silica of the same size, was packed to achieve a catalyst bed length of 80 mm. Thus, the catalyst bed was extended 30 mm, as illustrated in the inset of Fig. 1. The MR was inserted into an electronic heating furnace controlled by a temperature controller/programmer. The fuel feedstock is a mixture of liquid hydrocarbons with carbon numbers in the range of 4–8 (light distillate of Daqing F–T plants, simplified as fuel in the following text). The average molecular formula of the fuel was $C_{6.43}H_{14.84}$ and the molecular weight 92.0 g mol^{-1}. Fuel and water were metered and delivered to the evaporator by HPLC pumps. After evaporation and mixing at 573 K; they were preheated to about 723 K before entering the reactor. H_2 was also fed to the reaction at a hydrogen-to-carbon molar ratio (H_2/C) of 0.1. The flux of H_2, or sweep gas Ar were controlled by mass flowmeter (Brooks Instrument 5850S). Prior to reaction, the catalyst was heated in a pure Ar flux of 50 cm^3 min^{-1} at a rate of 2 K min^{-1} to 673 K to avoid the H_2 embrittlement of the Pd Membrane. Then a 30% (v/v) H_2–Ar gas stream of 200 cm^3 min^{-1} was introduced and the temperature was further increased to 823 K at a rate of 2 K min^{-1} and kept for 3 h. The gas compositions in the reaction side, or those in the permeate side were determined by an online Varian CP-3800 GC equipped with TCD (thermal conductivity detector) and FID (flame ionization detector). Ar was the carrier gas for the GC, so the purity of H_2 in the permeate side, with or without sweep gas, can be determined (if sweep gas was applied, the calculation of H_2 purity does not take it into account). Under the experimental conditions, no higher hydrocarbons in the products were detected. Thus, the

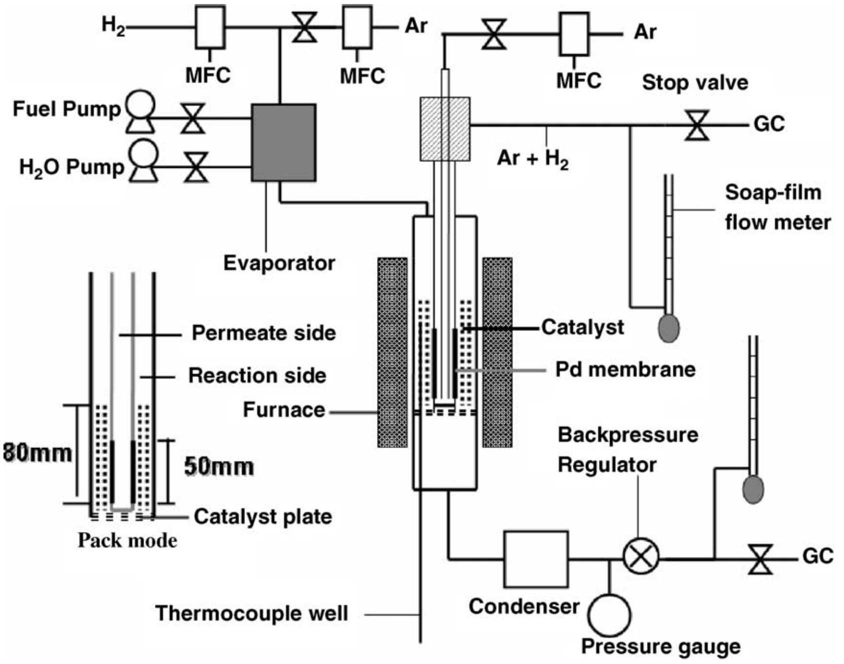

Fig. 1. Schematic diagram of reaction and analysis system for the steam reforming of liquid hydrocarbons in the palladium membrane reactor.

conversion of fuel is supposed to be 100%. On the calculation of the reaction GHSV, fuel flux is converted to the equal methane flux (F_{CH_4}) based on the carbon balance according to:

$$F_{CH_4}\,(\mathrm{ml/min}) = \frac{\text{flux of } C_{6.43}H_{14.84} \times \rho \times 6.43}{92} \times 22,400 \tag{4}$$

where, ρ was the average density of fuel (g cm^{-3}), the unit for the flux of $C_{6.43}H_{14.88}$ is ml min^{-1}. And yield of H_2 (Y_H), yield of CH_4 (Y_M), sweep ratio (I) and H_2 recovery rate (R_H) are defined or calculated by the following equations:

$$Y_H = \frac{\text{molar hydrogen produced}}{\text{molar fuel feed}} \tag{5}$$

$$Y_M = \frac{\text{molar methane produced}}{\text{molar fuel feed}} \tag{6}$$

$$I = \frac{\text{flux of sweep gas}}{F_{CH_4}} \tag{7}$$

$$R_H = \frac{H_2 \text{ flux across the Pd membrane}}{H_2 \text{ production rate} + H_2 \text{ flux in the feed}} \times 100\% \tag{8}$$

Simultaneously, the flux of the gas in the permeate side, and those from the outlet of the PMR were measured by soap film flowmeter after the condensing of the steam.

3. Results and discussion

3.1. Palladium membrane properties

The H_2 permeance and H_2/N_2 separation coefficient of the Pd membrane were determined with pure N_2 and H_2 at 773 K and transmembrane pressure of 100 kPa. The membrane has a H_2 permeance of 50 m^3 m^{-2} bar^{-1} h^{-1}, a H_2/N_2 separation coefficient of 1200. The membrane thickness is estimated about 4.5 μm based on the weight increase after the plating process. Comparison with some literature data was made [13], and the results are listed in Table 1. From the results, it could be concluded that the developed membrane has a high H_2 permeance and a good H_2/N_2 separation coefficient.

3.2. Back permeation of hydrogen and its suppression

Usually, pure H_2 is the desired product in steam reforming. Thus, sweep gas in the permeate side cannot apply, except using steam at low sweep ratios [20]. In addition, vacuum application, is also unlikely due to its high energy consumption. When no sweep gas was applied, to obtain H_2 permeation through all the membrane area from the reaction side to the permeate side, the local partial pressures of H_2 near the interface of the membrane in the reaction side should exceed 101.3 kPa. However, in the steam reforming of liquid hydrocarbons, S/C ratios are usually >2.0 to avoid coke deposition. Such reaction conditions correspond to over 90 mol% steam at the inlet of the catalyst bed. Thus, if the length of catalyst bed equals that of the Pd membrane, back permeation of H_2, as illustrated in Fig. 2, necessarily takes place near the inlet of the catalyst bed. This back permeation of H_2 becomes a disadvantage in terms of R_H and the efficient utilization of the membrane. Generally, three ways could be applied to avoid this phenomenon. (1) Using a sweep gas. However, it reduces the concentration of H_2. (2) The addition of H_2 in the feedstock. However, as suggested by Chen et al. [21], H_2 partial pressure has great influence on the kinetics and thermodynamic equilibrium of *n*-heptane steam reforming. Higher H_2 partial pressures in the feedstock decrease not only the reaction rate but also Y_H. Thus, although a low

Table 1
H_2 separation efficiency of the Pd membrane in this work and comparison with previous results [13]

Mem	Pre-method	Thick (μm)	T (K)	DF (kPa)	H_2 flux (mol m^{-2} s^{-1})	Sepn factor
Pd/MPSS	ELP/O	10	753	100	0.089	1000
Pd/MPSS	ELP	19–28	773	100	0.015–0.023	<5000
Pd/MPSS	ELP	5	673	100	0.155	100
Pd/PG	ELP	13	773	202	0.189	∞
Pd/Al_2O_3	ELP	7–15	673	100	0.086–0.134	100–1000
Pd/HF	ELP	3–4	703	100	0.136	1000
Pd/Al_2O_3	CVD	0.5	623	100	0.05	500
Pd–Ag/PG	EFP	21.6	673	202	0.067	∞
Pd–Ag	CR	50	773	100	0.01	∞
Pd/MPSS	MDELP	6.0	773	100	0.26	∞
This work	MELP	4.5	773	100	0.62	1200

ELP: electroless plating, MPSS: macroporous stainless steel, HF: hollow fiber, DF: permeation driving force, CR: cold rolling, MDELP: multidimensional plating mechanism, MELP: modified electroless plating.

concentration of H_2 in the feedstock may enhance the reaction rate, it is not sufficient to suppress the back permeation of H_2. A higher partial pressure of H_2 in the feedstock slows the reaction rate, at the same time enhancing the formation of CH_4 instead of H_2. Moreover, it is probable that H_2 in the feedstock could not be efficiently recovered by the membrane. (3) Using an extended catalyst bed. It makes the steam and higher hydrocarbons react before contacting the membrane area, achieving an H_2 partial pressure higher than 101.3 kPa. A higher performance of the PMR could be expected by using such a MR configuration, which had been experimentally demonstrated in methane steam reforming using a PMR [22]. Actually, the simulation work by Chen et al. [17] indicated that, in a CFBMR with a catalyst bed length of 2 m, the necessary catalyst bed length for the complete conversion of *n*-heptane is only 0.3 m at 823 K. As the steam reforming of higher hydrocarbons is irreversible, and the methanation and WGS reactions reach their equilibrium as soon as the higher hydrocarbons are fully converted. The selective removal of H_2 is supposed to break the thermodynamic equilibrium of methane steam reforming and WGS reactions, which continue to take place in the rest of the reactor. Thus, ideally, the MR should be designed in such a way that the catalyst in the extended part is just sufficient for the complete conversion of higher hydrocarbons. Therefore, both the catalyst and the membrane could be efficiently utilized in the PMR.

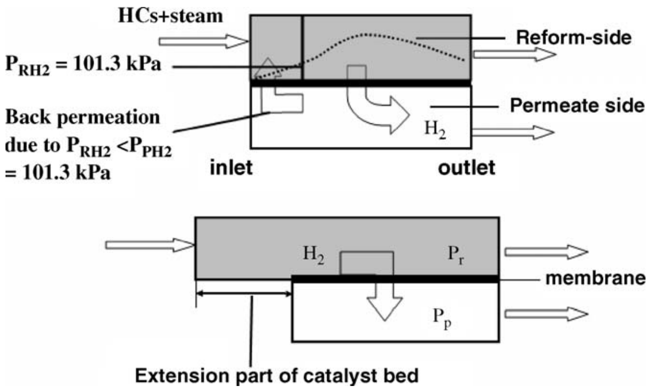

Fig. 2. Back permeation of H_2 in the steam reforming of higher hydrocarbons in a membrane reactor and proposed way to prevent it (HCs: higher hydrocarbons, P_{RH2}: H_2 partial pressure in the reaction side, P_{PH2}: H_2 partial pressure in the permeate side).

3.3. Influence of working conditions on the performance of membrane reactor

3.3.1. Influence of reaction GHSV

The influence of reaction GHSV on Y_H and R_H were investigated at $T = 823$ K, S/C = 2.7 and H_2/C = 0.1. Fig. 3 shows the results. Increasing reaction GHSV leads to lower Y_H and R_H in the PMR. For instance, Y_H decreased from 11.2 to 10.4 at $P = 500$ kPa, from 14.1 to 11.8 at $P = 700$ kPa and from 15.9 to 12.1 at $P = 900$ kPa with an increase of GHSV from 7500 to 15,000 ml g^{-1} h^{-1} when no sweep gas was applied, as shown in Fig. 3(a). At the same time, increasing reaction GHSV results in a decrease of R_H. For instance, R_H decreased from 58.0% to 38.9% at 500 kPa, from 70.8% to 62.3% at 700 kPa and from 81.3% to 73.7% at 900 kPa, respectively, as shown in Fig. 3(b). Higher reaction GHSV leads to a shorter residence time, which is disadvantageous for the generated H_2 to diffuse from the reaction zone to the Pd membrane interface, and the virtual H_2 pressure drop across the membrane decreased. Therefore, lower Y_H and R_H are obtained at a higher reaction GHSV. However, a higher GHSV promises a higher H_2 production capacity for the PMR. For instance, when other working conditions were the same, although R_H and Y_H obtained at GHSV = 15,000 ml g^{-1} h^{-1} and $I = 1.0$ were obviously lower than those obtained at GHSV = 7500 ml g^{-1} h^{-1} and $I = 1.8$, the H_2 production capacity of the PMR was 23.1 m^3 m^{-2} h^{-1} in the former case, still higher than the one of 19.0 m^3 m^{-2} h^{-1} in the latter case. This agrees with the previous results in the methane steam reforming using PMRs. For example, Kikuchi et al. [23] found that increasing reaction GHSV resulted in a decrease of methane conversion, too. Lin et al. [24] predicted the influence of the weight hourly space velocity (WHSV) on the methane conversion by simulation. The results also indicated that methane conversion gradually decreases with increasing WHSV. The agreement indicates that owing to the irreversibility of the steam reforming of higher hydrocarbons, the selective removal of H_2 mainly breaks the thermodynamic equilibrium of methane steam

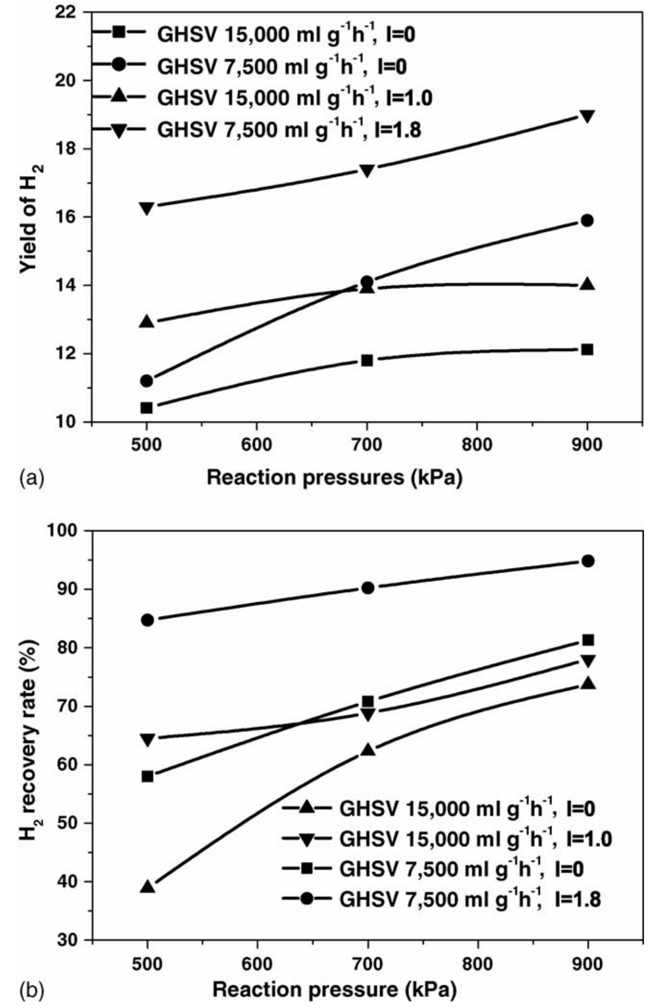

Fig. 3. Influence of GHSV on the yield of hydrogen (a) and on the hydrogen recovery rate (b) ($T = 823$ K, S/C = 2.7, H_2/C = 0.1).

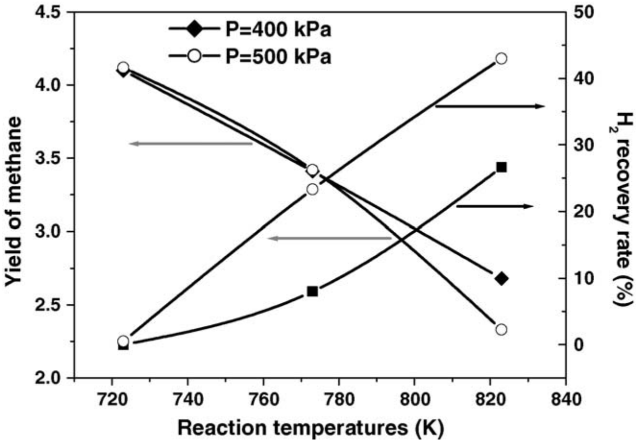

Fig. 4. Influence of reaction temperature on the H_2 recovery rate and on the yield of methane in the palladium membrane reactor (GHSV = 15,000 ml g^{-1} h^{-1}, S/C = 2.7, H_2/C = 0.1 and $I = 0$).

reforming and WGS. In this work, as the highly active catalyst [19] and an extended catalyst bed was applied, higher hydrocarbons may be completely converted before entering the following reaction zone in close contact with the Pd membrane. So the results achieved in this work, are comparable with those obtained in the steam reforming of methane in MRs. In this work, a high performance Pd membrane, a highly active steam reforming catalyst combined with a countercurrent sweep gas design, gave a Y_H value of 19.0, a R_H value of 94.8% and a Y_M value of 0.37 at $T = 823$ K, $P = 900$ kPa, GHSV = 7500 ml g^{-1} h^{-1}, S/C = 2.70 and $I = 1.8$. In contrast with the best results obtained in methane steam reforming in PMR [13], i.e. a methane conversion of 97% was achieved at $T = 823$ K, $P = 500$ kPa, GHSV = 800 ml g^{-1} h^{-1}, S/C = 3.0 and $I = 10$, the GHSV applied in this work was much higher, and the sweep ratio was much lower. These characteristics suggest that the PMR could be operated under working conditions closer to the practical application ones.

3.3.2. Influence of reaction temperature

The influence of reaction temperature on Y_M and R_H were studied at $T = 723$–823 K, $P = 400$ or 500 kPa, S/C = 2.7, GHSV = 15,000 ml g^{-1} h^{-1} and $I = 0$. Fig. 4 shows the results. It indicates that R_H increases, while Y_M decreases with an increase in reaction temperature. At 723 K, there was no H_2 detected in the permeate side. The Y_M in the PMR was 4.10 at 400 kPa, and 4.12 at 500 kPa. This agrees with the simulation work by Chen et al. [17], which suggested that at 723 K, the thermodynamic equilibrium of methanation could not be efficiently broken in the *n*-heptane steam reforming, and H_2 could not be efficiently recovered by the membrane. At $T = 773$ K, H_2 in the permeate side was detected, but R_H was small, with values of 8.0% at $P = 400$ kPa and 23.3% at $P = 500$ kPa. The Y_M reduced to values of 3.42 at 400 kPa and 3.41 at 500 kPa, respectively; versus thermodynamically controlled ones of 4.02 at 400 kPa, and 4.14 at 500 kPa. The small flux of H_2 across the membrane and low separation efficiency resulted in only a slight decrease of Y_M in the PMR. R_H increased, while Y_M decreased significantly with further increase of reaction temperature to 823 K. For instance, at $P = 400$ kPa, the R_H, Y_M obtained in the PMR and the thermodynamically controlled Y_M in CFBR were 26.6%, 2.66 and 3.35, respectively. They became 43.0%, 2.32 and 3.50 at $P = 500$ kPa, respectively. The decrease of Y_M in PMR is a result of the thermodynamic equilibrium shift due to the selective removal of H_2 from the reaction zone. Though higher reaction temperatures favor the Y_H and R_H, further increase is unlikely because: (1) Catalyst deactivation may become a problem under reaction conditions with high R_H. In the steam reforming of higher hydrocarbons, when a nickel-based catalyst was applied, the higher the reaction temperature, the higher the critical S/C ratios (a steam-to-carbon feed ratio under which value coke deposition on catalyst takes place). Higher S/C ratios increase the energy consumption, and decrease the energy efficiency of the fuel processor and the membrane separation efficiency. (2) Sintering of the nickel-based catalyst may happen. (3) Higher temperature may degrade the applied Pd membrane. So, the steam reforming of methane or higher hydrocarbons in the PMR was usually investigated in the temperature range of 723–823 K. The above results also suggested that at lower reaction pressures, when no sweep gas was applied, H_2 could not be efficiently recovered due to the limited H_2 permeation driving force. So the optimization of other working conditions was investigated at 823 K.

3.3.3. *Influence of steam-to-carbon feed ratios*

Steam reforming of higher hydrocarbons is usually performed in the presence of an excess of steam to suppress the coke deposition on a nickel-based catalyst. In the industrial steam reforming of naphtha, S/C ratios in the range of 2.0–4.0 are applied. So, in this work, the influence of S/C ratios on the Y_H, R_H and net yield of H_2 (Y_H multiplied by R_H), were investigated at $T = 823$ K, $P = 400$ kPa, $F_{CH_4} = 180\ \text{ml min}^{-1}$, $H_2/C = 0.1$, $I = 1.0$ and S/C ratios in the range of 2.0–3.6. Fig. 5 shows the results. It was found that a higher S/C ratio promoted the H_2 production, but it was not the case with the net yield of H_2. The lower R_H obtained at a higher S/C ratio, was attributed to the fact that H_2 partial pressures in the reaction side and separation efficiency decreased due to the dilution effect of steam. Thus, the net yield of H_2 is a compromise between the enhanced Y_H and decreased R_H when S/C ratios increased. For instance, Y_H increased from 15.2 to 15.9 when the S/C ratio increased from 2.7 to 3.6. However, the net yield of H_2 decreased from 12.16 to 11.59, simultaneously, R_H decreased from 80.0% to 72.9%. This agrees with the results reported by Shu et al. [25], who gave a detailed study of the influence of S/C ratios on the methane conversion in the steam reforming of methane by using Pd/SS or Pd–Ag/SS-based MR. They found that methane conversion increased with increasing S/C ratios. However, the net yield of H_2 showed a non-monotonic relation with S/C ratios. In this work, a net H_2 yield of 12.16 obtained at S/C = 2.7 was the highest one. The results suggest that too large an excess of steam dilutes the H_2 in the products mixture, which results in a decrease of the H_2 partial pressure drop across the membrane and thus in a lower separation efficiency of the membrane. Therefore, in the optimization of S/C ratios, at least two factors should be considered. (1) S/C ratios should be high enough to prevent coke deposition on the catalyst. (2) As Y_H increases, while R_H decreases with increasing S/C ratios, a compromise should be made between the two opposing factors. Simulation results obtained in CFBMR [21] suggested that it is possible to make the steam reforming of higher hydrocarbons in the PMR coke-free when S/C ratios higher than 2.5 were applied. So, in this work, a S/C ratio of 2.7 was applied and under such conditions, no coke deposition on the catalyst was detected, and high net yield of H_2 was achieved.

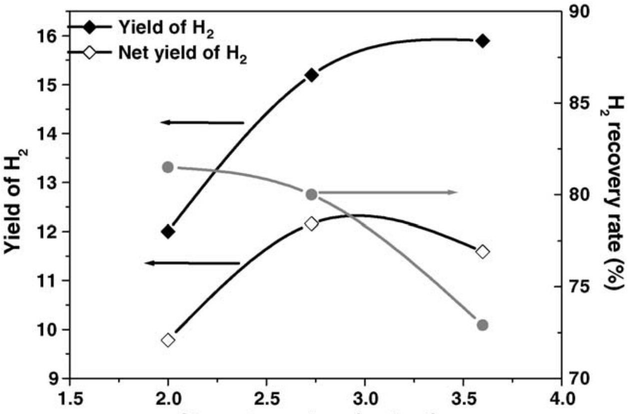

Fig. 5. Influence of the steam-to-carbon feed ratio on the yield of hydrogen in the PMR, on the net yield of hydrogen and on the hydrogen recovery rate ($T = 823$ K, $P = 400$ kPa, $F_{C1} = 180\ \text{cm}^3\ \text{min}^{-1}$ and $I = 1.0$).

3.3.4. *Influence of reaction pressure*

The influence of reaction pressure on the performance of the PMR was investigated widely. In this work, a non-monotonic change of methane yield with reaction pressure was found in the pressure range of 200–900 kPa at $T = 823$ K. The results presented in Fig. 6 clearly indicate that at higher pressures Y_M is effectively decreased when pressure increases, for $P = 500$–900 kPa and $I = 0$. In CFBR, Y_M increases monotonically from 2.8 to 3.9, when reaction pressure increases from 200 to 900 kPa at 823 K, being controlled by the thermodynamic equilibrium. Because 3 mol of H_2 is consumed to produce 1 mol of methane via the methanation reaction, the yield of H_2 deceased quickly due to the methane formation. In the PMR, this trend was firstly kept in the pressure range of 200–400 kPa, being reversed at 500–900 kPa, e.g. methane yield decreased with reaction pressure apparently. The Y_M was further reduced by using a countercurrent sweep gas. At lower reaction pressures, the use of sweep gas reduced Y_M more efficiently. For example, at $T = 823$ K, $P = 400$ kPa, GHSV = 15,000 ml $g^{-1}\ h^{-1}$, S/C = 2.7, $H_2/C = 0.1$, the Y_M was 2.69 at $I = 0$ and it decreased to 1.88 at $I = 1.0$; while at $P = 900$ kPa, the value of Y_M was 1.73 at $I = 0$ and it only slightly decreased to 1.35 at $I = 1.0$. The Y_M values obtained in the PMR are much lower than the thermodynamically controlled ones. In this work, Y_H improvement as high as 300%, in comparison with the thermodynamically controlled one was achieved. For instance, at $T = 823$ K, $P = 900$ kPa, GHSV = 7500 ml $g^{-1}\ h^{-1}$ and $I = 0$, Y_M, Y_H and R_H values were 0.99, 15.9 and 81.3%, respectively. The best results in this work, i.e. Y_M of 0.37, Y_H of 19.0 and R_H of 94.8%, corresponding to a net pure H_2

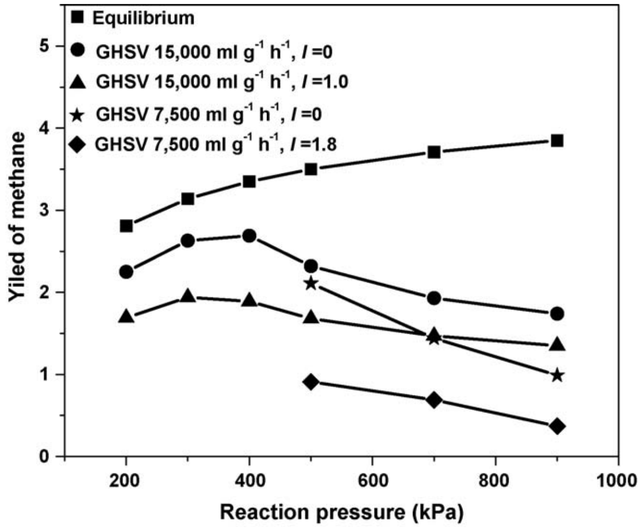

Fig. 6. Methane yields obtained in the palladium membrane reactor as a function of reaction pressure and their comparison with thermodynamically controlled values ($T = 823$ K, S/C = 2.7 and $H_2/C = 0.1$).

production of 88.9% of the theoretical maximum H_2 production (supposing 100% selectivity to CO_2), were obtained at $T = 823$ K, $P = 900$ kPa, GHSV = 7500 ml g^{-1} h^{-1} and $I = 1.8$, while the thermodynamically controlled Y_H is only 4.9. Chen et al. [21] also predicted that Y_H increased with increasing reaction pressures for the *n*-heptane steam reforming in a novel CFBMR, by simulation. The value of 19.34 for Y_H was predicted at $T = 823$ K and $P = 1023$ kPa. Comparable results were obtained in our work. To sum up, the trend that higher reaction pressures promote Y_M instead of Y_H in CFBR is reversed by selective H_2 removal from the reaction zone, which makes it feasible to achieve acceptable Y_H at higher reaction pressure and at lower temperature, instead of high temperature in the traditional naphtha steam reforming. This eliminates the complex downstream processing of CO and further H_2 purification. H_2 production could be realized using only one highly integrated PMR, which was coupled the highly active steam reforming catalyst and the highly H_2 permeable membrane.

3.3.5. *Influence of sweep gas flux*

Introducing a sweep gas in the permeate side is an efficient method to increase the H_2 partial pressure drop across the membrane, thus promoting the H_2 permeation and improving the R_H. When pure H_2 is the desired product, sweep gas types should be chosen carefully. Generally, from a practical application point of view, using steam at a low sweep ratio is acceptable [20]. If the fuel processor is in situ coupled to a fuel cell, using steam as sweep gas, the requirement of H_2 humidification in PEMFC is met. The influence of sweep gas flux on the performance of the MR is also closely related with the MR operation modes: cocurrent or countercurrent [21]. In this work, a H_2 permselective membrane was used under countercurrent operation. The influence of sweep gas flux on Y_H and R_H was investigated at $T = 823$ K, $P = 400$ kPa, GHSV = 7500 ml g^{-1} h^{-1}, S/C = 2.7 and H_2/C = 0.1, and the results are shown in Fig. 7. A higher sweep gas flux promoted the H_2 production, but this trend became not so obvious at $I > 2.0$. The results obtained at $I = 0$ differed much from those obtained at $I = 1.0$, i.e. Y_H values increased from 9.95 to 15.2 and R_H values from 41.4% to 75.0%. However, only a slight improvement was obtained with further increase in the sweep ratios from 1.1 to 4.2, i.e. Y_H values from 15.2 to 17.0 and R_H values from 75.0% to 82.0%, were obtained. In methane steam reforming using PMR, Uemiya et al. [11], Lin et al. [12] and Gallucci et al. [20] also found that a higher methane conversion could be obtained at a higher sweep ratio, and the increase in methane conversion became less and less at higher sweep ratios. Actually, Shu et al. [25] found that when $I > 3.25$, no further increase of methane conversion was found. This means that a continuous increase of sweep flux plays only a minor role in enhancing the Y_H and R_H. Dittmeyer et al. [26] studied the influence of the sweep gas flux on the H_2 permeation in detail. They found that when too large a sweep gas flux is applied, no real improvement of the H_2 permeation flux is observed, even at higher retentate pressures (i.e. high H_2 feed flux).

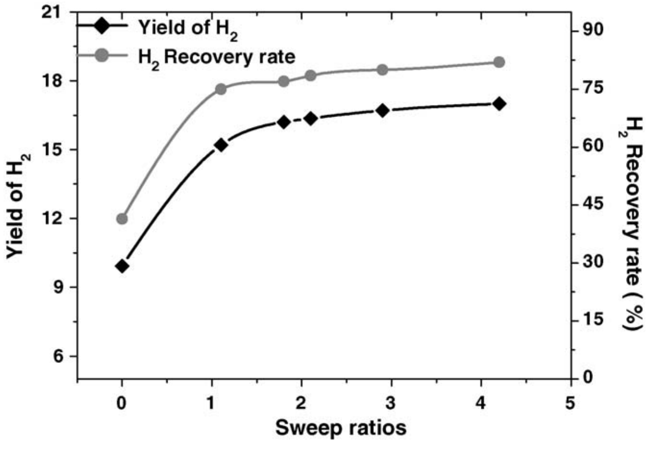

Fig. 7. Influence of sweep ratio on the yield of H_2 and H_2 recovery rate in the palladium membrane reactor ($T = 823$ K, $P = 400$ kPa, GHSV = 7500 ml g^{-1} h^{-1}, S/C = 2.7 and H_2/C = 0.1).

The performances of the PMR are closely related to the working conditions, such as reaction temperature, GHSV, S/C ratio, reaction pressure and sweep gas flux. In this work, from an industrial point of view, H_2 production was investigated under working conditions close to the practical application ones, such as relative high GHSV and low flux of sweep gas, or without sweep gas. It was found that H_2 still could be efficiently produced by using a relatively higher reaction pressure at temperatures lower than 823 K. After reaction for 30 h under various conditions, no degradation of the Pd membrane was observed. The H_2 permeance and the H_2/N_2 separation coefficient of the membrane showed almost no change. Thus, the process has promising stability and further investigation is under way.

4. Conclusions

Back permeation of H_2 in the steam reforming of liquid hydrocarbons in PMR, has been successfully avoided by using an extended catalyst bed. The yield of methane could be significantly suppressed, while the yield of H_2 efficiently enhanced by the selective removal of H_2 from the reaction through the highly H_2 permeable Pd membrane. Higher reaction temperatures favor the yield of H_2 and H_2 recovery rate in the range of 723–823 K. Increase in the S/C ratios increases the yield of H_2. However, identical behavior has not been observed for the H_2 recovery rate. The net yield of H_2 is a compromise between the two opposing factors. Optimal S/C ratio was found to be around 2.5. Lower GHSVs favors the yield of H_2 and recovery rate but not the H_2 production capacity of the PMR. Most importantly, the trend that the yield of methane increases with reaction pressures in CFBR is reversed by the selective H_2 removal in PMR, which makes it feasible to achieve a pure H_2 production process using only one MR. In summary, under mild working conditions, a low-emission H_2 production process by the steam reforming of liquid hydrocarbons in PMR was proposed and successfully demonstrated. This process may find its unique application to small-scale H_2 production using the readily available infrastructure.

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